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Effects of Co-Solvents on the Partition Coefficient of Hydrophobic Organic Compounds

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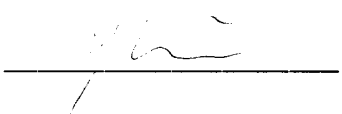

Acknowledgements

I would like to thank Kathi Kimble, Doug Errett , and Yo Chin for all the help that they have given me in the past year. Without their help I would not be where I am today. I would like to thank Kathi and Doug for training me on all the equipment in the laboratory and for their help with the batch experiments.

Abstract

Hydrophobic organic compounds (HOCs) pose a major threat to aqueous systems. The tendency for HOCs to sorb onto soil organic matter makes them less accessible for remediation with traditional pump and treat techniques. As a result, many "treated" aquifers remain contaminated after their purported remediation. The addition of alcohol solvents into the aqueous system can enhance the movement of the HOCs. Isotherm batch experiments were used to find values of the equilibrium partition coefficient for the commonly found HOCs through the following relationship, $Cs = K_p Ce$ where Cs and Ce are the equilibrium solid phase and liquid phase concentrations respectively. The results of our experiments show that there is a definite increase in solution phase concentration (i.e. decrease in K_p of the organic compounds when the methanol concentration in the solution phase was increased. Thus, we believe methanol can be used as an additive to enhance the removal of HOCs from tainted aquifers.

Introduction

Contaminated groundwater poses a major threat in the United States. Communities that rely on groundwater for daily use may rely on a water supply that has become contaminated. Consumption of contaminated groundwater can lead to serious health problems. Younger children and infants are the most effected by the pollutants. Contaminated rivers and lakes also pose major threats to indigenous organisms living in these systems.

Processes such as photodegradation and biodegradation tend to lower the concentration of hydrophobic organic compounds (HOCs) in the aquatic environment. However, sorption of the HOCs prevent or slow down these processes. The high tendency for HOCs to become sorbed, interferes with biodegradation due to inaccessibility of the compound. Organic matter shades the HOCs from any light that can break them down.

Predicting the fate and transport of organic contaminants in aquatic environments depend greatly on their distribution between a solid (i.e. soils,sediments, and biota) and aqueous phase. Polycyclic aromatic hydrocarbons (PAHs) are common surface and groundwater pollutants that are hydrophobic by nature and are sparingly soluble in water. The propensity for these substances to be sorbed by soils and sediments is strong and their movement in an aquifer is often retarded. Understanding sorption is important when assessing the transport of organic contaminants through groundwater systems. Remedial techniques can then be applied once the movement and properties are understood. Traditional pump- and-treat methods prove to be inefficient when dealing with HOCs because they are strongly sorbed by soil/sediment organic matter and are immobile. Pump- and- treat

methods only remediate the contaminated pore fluids and the source areas are not treated.

The addition of co-solvents (water miscible compounds) such as alcohols can enhance the mobilization of HOCs sorbed by soils and sediments. The co-solvents lower the pore-fluid surface tension of water and can enhance HOCs solubility. Co-solvents can decrease the sorption of the organic compounds, making them more mobile.

The objectives for my research were to study sorbent chemistry (i.e. properties of soils and sediments) on sorption. One sediment and two soil samples were used in this study. Isotherm batch experiments were performed on the sediment and soil samples with three polycyclic aromatic hydrocarbons (methylnaphthalene, phenanthrene, and pyrene). Effects of co-solvents were studied with the same compounds, and soils. Solution chemistry was changed be adding low amounts of methanol (< 40% by volume).

Background Theory

The nature and abundance of carbon content of the sorbent defines the amount of partitioning of hydrophobic compounds between soils/sediments and the aqueous phase (Chiou et al, 1983). The equilibrium partition coefficient K_p can be normalized for the amount of organic carbon content of the soil or sediment by the following equation:

$$K_p = K_{oc}\, foc \qquad (1)$$

where K_{oc} is the octanol water partition coefficient and foc is the fraction of organic carbon present in the soil or sediment. Research has been done to find the K_{oc} values for many organic solutes. These values are constants and are well documented in the literature. The values that were used in designing our experiments came from Karickhoff and co-workers (1979).

Organic solutes are uncharged compounds that are attracted to the organic matter in soils and sediments. Mineral matter within soil sediments have a high polarity for which water molecules are highly attracted. It is this polar attraction between the mineral surface and water that controls the distribution of organic solutes between the solid and aqueous phase. The organic solute is uncharged therefore it can not compete with the water molecules for any empty mineral surfaces.

The partition coefficient K_p is directly proportional to the activity coefficient of the sorbate in the aqueous phase to that in the organic carbon phase. The addition of a co-solvent can change the aqueous activity coefficient of the sorbate which in turn will change the soil/sediment partition coefficient (Brusseau et al 1991, Fu and Luthy1986).

Partitioning effects of co-solvents on PAHs can be described by the following equation:

$$\log K_{oc} = \log K_{oc} - \alpha\sigma f_{cs} \qquad (2)$$

where K_{occ} is the normalized partition coefficient of the co-solvent water mixture, α is an empirical constant, f_{cs} is the volumetric fraction of co-solvent and σ is the solvency potential. Values for α are poorly documented in the literature. Values of α range from 0.51 to 0.9.

Materials and Methods

Sorption isotherm batch experiments were performed on methylnaphthalene, phenanthrene, and pyrene (Aldrich Chemicals in Milwaukee,WI.). All chemicals are 98% + pure. The glassware used in each experiment was washed in a five step process after each run and periodically cleaned with NOCHROMIX by Godax Laboratories, to oxidize any organic residue on the glassware. Washing of the glassware consisted of the following steps:

1.) A quick rinse with 100% methanol of HPLC grade to clean most of the organic compound from the glassware and also to protect the handler.
2.) Wash with warm tap water and ALCONOX detergent cleaner(VWR Scientific Inc.). Rinse three times with warm tap water.
3.) Rinse with distilled water three times.
4.) Rinse with 100% methanol up to three times depending on the hydrophobicity of the organic compound.
5.) Rinse with reverse osmosis treated water three times and then once with Milli-Q treated water.

Glassware was dried in an oven at a constant temperature of 100 degrees C.

Soils/Sediments

Rossburg,OH soil was used for methylnaphthalene and pyrene batch experiments. It is a silty loam with a foc of 1.33%. Fraction organic carbon content was measured on samples by the lost on ignition technique at 450 degrees C. The pH of the Rossburg soil is around 7.5. Phenanthrene experiments were performed on soil from Piketon,OH. This soil is a calcareous soil, comprised of glacial outwash. It has a pH of 7.44 and an foc of 1.26%. The Lake Michigan sediments are surficial sediments taken from box cores by the R/V Seward Johnson and then subcored using acrylic tubes. The foc of the bottom sediments were found to be 8.8%.

Experiments

Three polycyclic aromatic hydrocarbons were used in isotherm batch experiments. These PAHs were picked because they represent a wide range in polarity and are found as pollutants in surface and groundwater.

Stock solutions for each compound was made up in a suitable organic solvent. The solutions had a concentration of 1000mg of compound to 1 L. of solvent (methanol or acetonitrile) depending on the polarity of the analyte. Each solution was

prepared in 100 ml Pyrex volumetric flasks. The flasks were then parafilmed and wrapped with tin foil to prevent any photodegradation. Stock solutions were then stored in the refrigerator and new solutions were made every 2 to 3 weeks.

Partition coefficients were determined by batch experiment. Experiments comprised of adding a known amount of compound to the selected soil or sediment and then either a water or arbitrary water/ methanol mixture of some consistency was added to 50 ml Corex or Pyrex centrifuge tubes. Phenanthrene and methylnaphthalene concentrations ranged from 0-600 ug/ml and pyrene concentrations ranged from 0-90 ug/ml. Tin foil squares were used to line the centrifuge tube to minimize losses by sorption.

Buffered water solutions were used (5mMole $CaCl_2$ and 1mMole $NaHCO_3$) to obtain a pH of around 7.5. This pH value is similar to the natural pH present in Ohio groundwater. Each experiment consisted of 15 tubes: 1 as a blank which contained only the buffered water solution and soil, 7 tubes containing a known amounts of soil and PAH with 50 ml of buffered water, and 7 tubes which were used as controls and only the corresponding amount of PAH concentration and buffered water solution. Soil amounts used were to give equilibrium concentrations half as large as the original concentration. The amounts of sorbent required were estimated *a priori* by the flowing equation:

$$Sm = (C_o - C_e)(V)/(S) \qquad (3)$$

where Sm is the amount of soil needed in each tube to obtain 70-80% of the solubility(S). C_o and C_e are the initial concentration of sorbent and the equilibrium concentration respectively. These values are estimated using Karickhoff's equation (1979). Volume (V) is the amount of buffered water solution added to each tube. The amount of soil added depended on the foc of that particular soil and its aqueous solubility. Only mg quantities of Lake Michigan sediments were needed because of the high organic carbon content in the sediments. For the two soils that had very

similar foc content the amount of soil added was substantially more (gram quantities). Each tube was weighed and the given amount of soil was then added along with 50 ml of buffered water. The tubes were weighed again to determine exactly how much solution was added assuming density of 1g/ml of water. All tubes except for the blank were then spiked with a specified amount of PAH from the stock solution. Microdispensers (VWR Scientific Inc.) were used to spike the solutions. After spiking, the tubes were sealed and then wrapped with aluminum foil to prevent photodegradation and placed on a mechanical shaker at room temperature (22 degrees C) until equilibrium was reached (approximately 48 hours for methylnaphthalene and 72 hours for pyrene and phenanthrene). Standards were also made to obtain a calibration curve. Standards were made in Pyrex volumetric flasks and were used with the identical buffered water solution and stock solution. Standards were parafilmed, wrapped with aluminum foil, and set aside until equilibrium was attained.

After samples reached equilibrium, (48-72 hours) they were centrifuged for an hour at room temperature (22 degrees C) on a temperature controlled Beckman GS-6R Centrifuge (Palo Alto,CA). Corex tubes were centrifuged at ~2000 rpms were the Pyrex tubes (which used a weaker glass were centrifuged at lower rpms (~1400). Samples, controls, and standards were assayed on a SLM Aminco 500C Spectrofluorometer to obtain equilibrium concentrations in the aqueous phase. Some batch experiments were analyzed on a Waters HPLC with a 470 Scanning Fluorescene detector to corroborate our Spectrofluorometer results. Every soils and sediments from any third experiment was extracted with acetonitrile and assayed for the PAH to determine mass balances. The solution remaining in tube was pipetted off, and a known amount of methanol or acetonitrile (~10ml) was added. The tubes were then allowed to equilibrate for approximately 1-2 hours on the mechanical shaker. The samples were then centrifuged, the supernatent liquid drawn off and analyzed on the

Spectrofluorometer to obtain concentration of the sorbed compound.

Effect of co-solvents on sorption was determined by the addition of methanol to buffered water solution for 0,10,20,30,40 % methanol by volume. Known concentrations of PAHs were added to each tube.

Results

Plots of our data give a linear relationship between the equilibrium solid phase (Cs) and the equilibrium liquid phase concentration (Ce). This relationship is determined by the partition coefficient of the compound. Values of K_{oc} were found from the graphs by the use of linear-least -square curve fitting. K_{oc} was determined using Eq. 1. The regression coefficients (r^2) for all except for one, range from .8 to .99, most of the values are in the upper part of that range. The lowest values were obtained from samples on which this was the only run completed to date. All of the problems are not worked out for this particular sediment. Although nonzero intercepts were obtained on all graphs the regression coefficient illustrates linearity due to their closeness to unity.

Soil and sediment partition coefficients differ from one another as seen in Figure 1. This graph illustrates the difference in the foc contents of the soil vs. sediments. As the graph illustrates there is a direct relationship of higher K_p values to higher foc content. The Lake Michigan sediment has an foc of 8.8% which is considerably higher than the 1.33% for the Rossburg soil. The K_p value for the sediment is greater by a factor of two. Therefore we can conclude that higher focs give higher partition coefficients. Figures 1- 3 relate the soil and sediment properties for three HOCs. All data was taken from isotherm batch experiments.

Karickhoff (1979) describes a relationship of the octanol water partition coefficient (K_{ow}) and the organic carbon partition coefficient. The following equation is based on his research:

$$\log K_{oc} = \log K_{ow} - .21 \quad (4)$$

Figure 4 is a plot of log K_{oc} vs. log K_{ow} for both the sediment and soils. The slope of the line is almost unity. The equation of our plot is slightly off from Karickhoff equation

$$\log Koc = .984 \log Kow - .792 \quad (5)$$

The intercept that on the graph is almost one which is considerably higher. However, I believe our sorption coefficients exhibited the same trends seen by Karickhoff.

Significant decrease in the partition coefficient were noticed when the methanol concentration was increased in our isotherm batch experiments. Figures 5 - 11 illustrate this decrease in partitioning into the organic matter of soil. Batch isotherm experiments were conducted on methylnaphthalene, phenanthrene, and pyrene. To study the effects of co-solvents methanol was added at 0,10,20,30 % by volume. Plots of the fraction of co-solvent (fcs) demonstrate a trend where Kp decreases with increasing fcs. Through the linear curve fit, σ values where obtained for all three of the compounds. These values correlated well with literature values when value of .50 was used for α. Throughout the literature have a wide range in α values are given. Karickhoff found α to range from .83 to .921. Fu and Luthy (1986) reported values much lower than that of Karickhoff. Their α value from a wide range of data was .51. Our data agrees with the smaller values, which are some what less than unity. We obtained these values from the slopes of the plots (Figures 9-11).

Addition of co-solvents into aquatic systems for remedial purposes is very feasible. Flooding of contaminated sites with water and low concentrations of alcohol can provide a better means for cleaning and reducing contaminants to target concentrations for easier cleanup.

Conclusion

Fate and transport of hydrophobic compounds in aqueous systems can be changed by the presence of co-solvents. Organic alcohols can increase the movement of HOCs through groundwater systems. It is this increased mobility that may enable the use of co-solvents in remedial techniques. Flushing an area with small amounts of alcohol and water can remove any contaminants where pump and treat methods could not.

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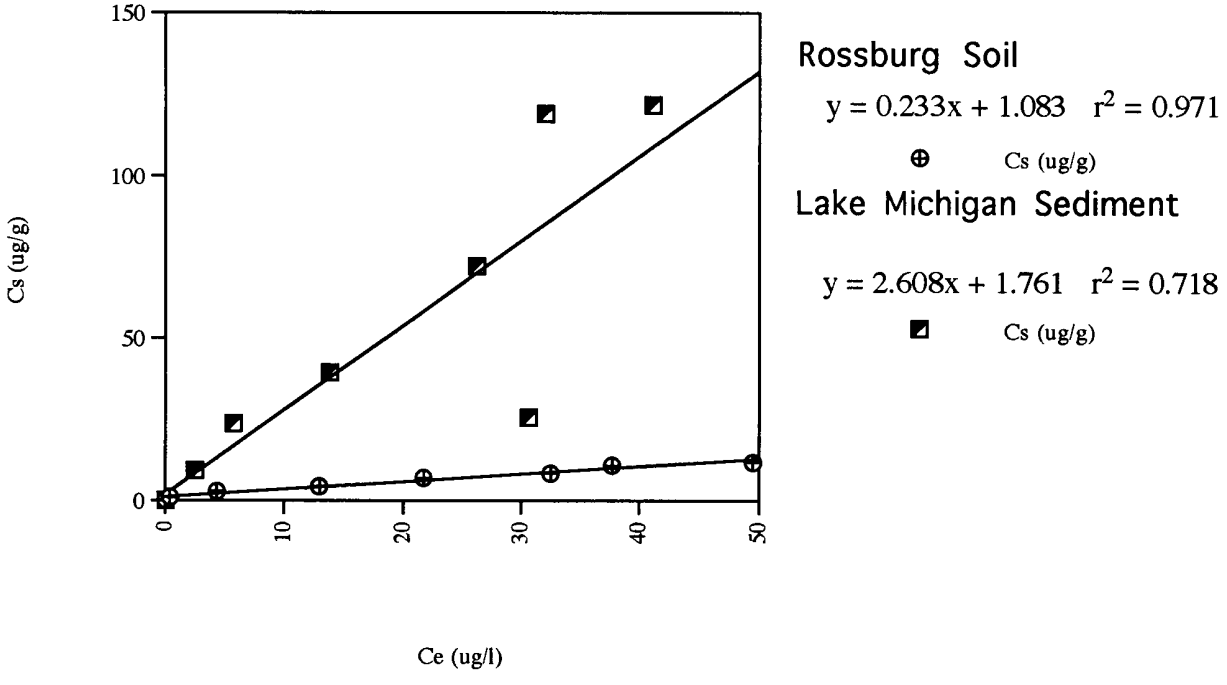


Figure 1: Comparison of Lake Michigan Sediment and Rossburg Soil for Pyrene sorption.

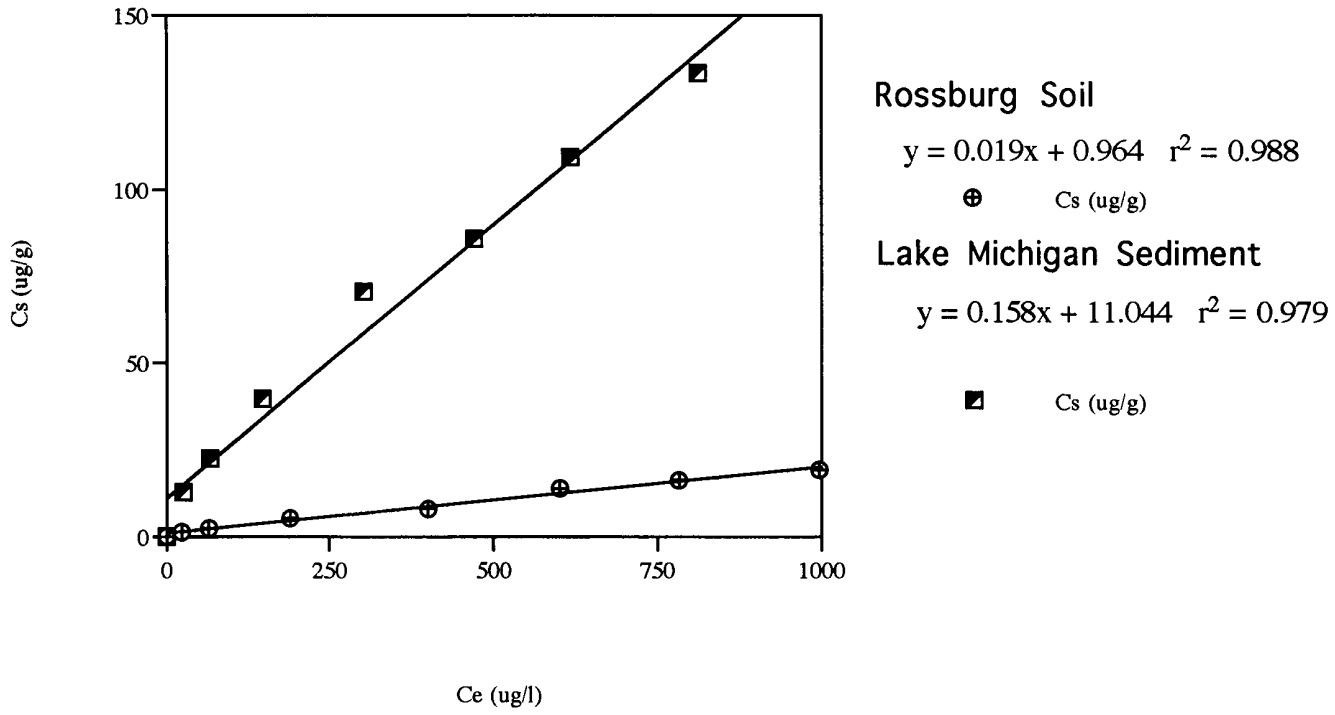


Figure 2: Comparison of Rossburg Soil and Lake Michigan for methylnaphthlene sorption.

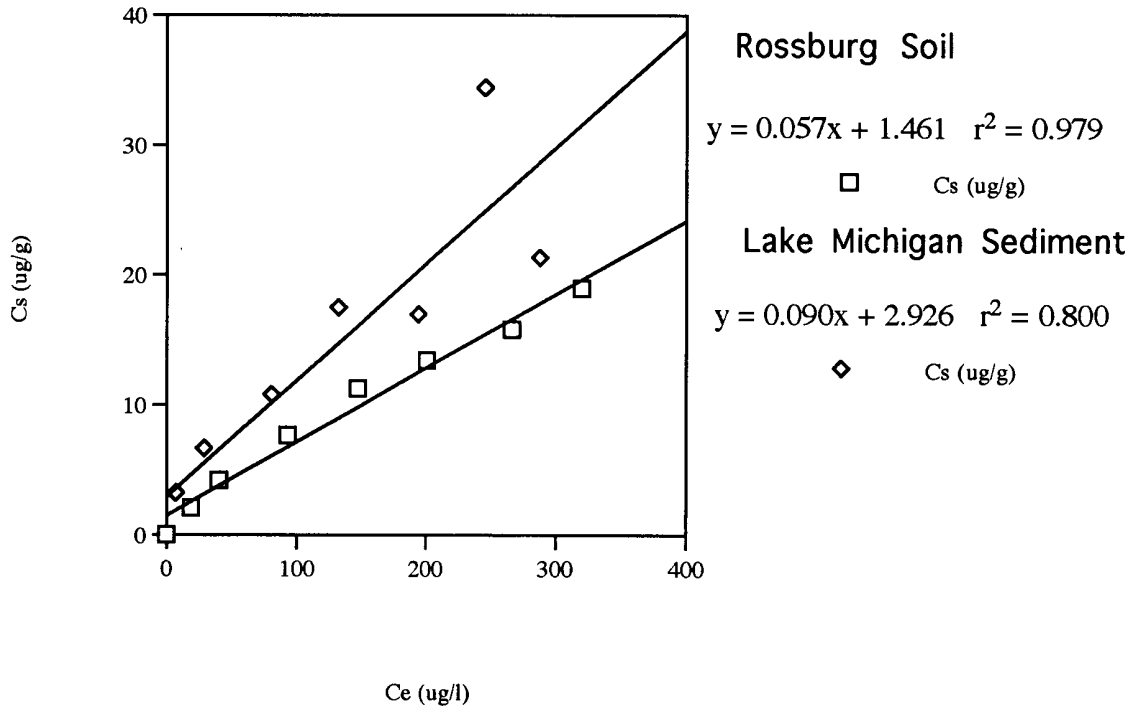


Figure 3: Comparison of Rossburg and Lake Michigan Sediment with phenanthrene sorption.

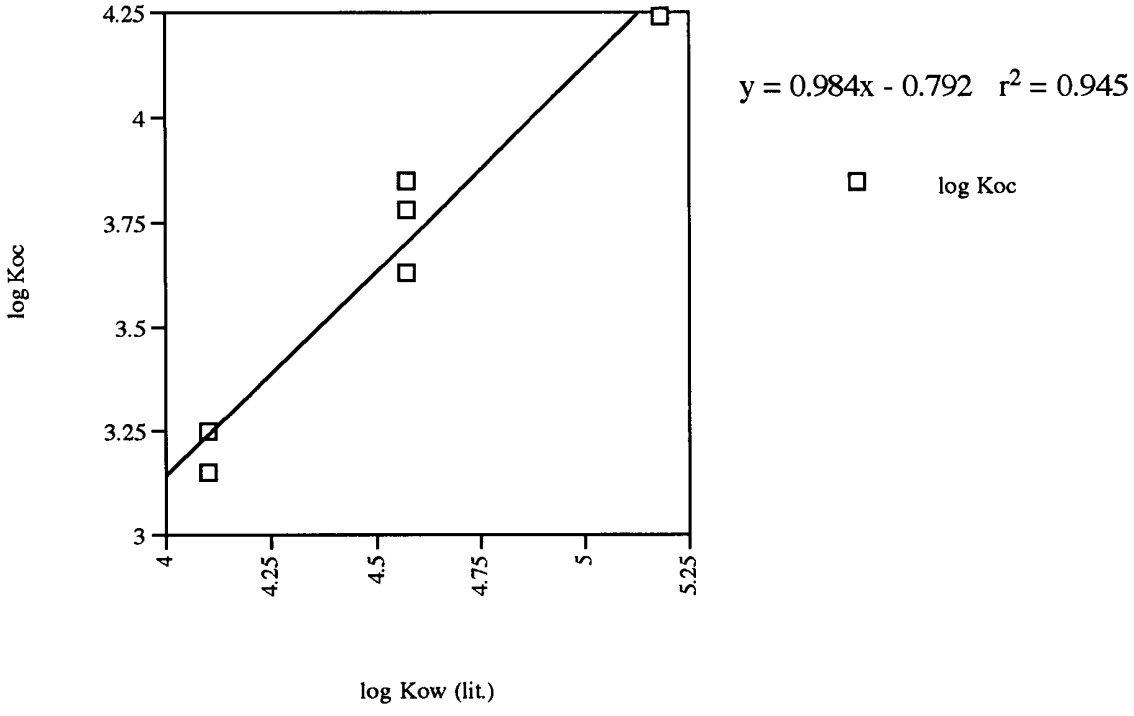


Figure 4: Relationship between Kow and Koc for soil and sediment experiments with HOCs.

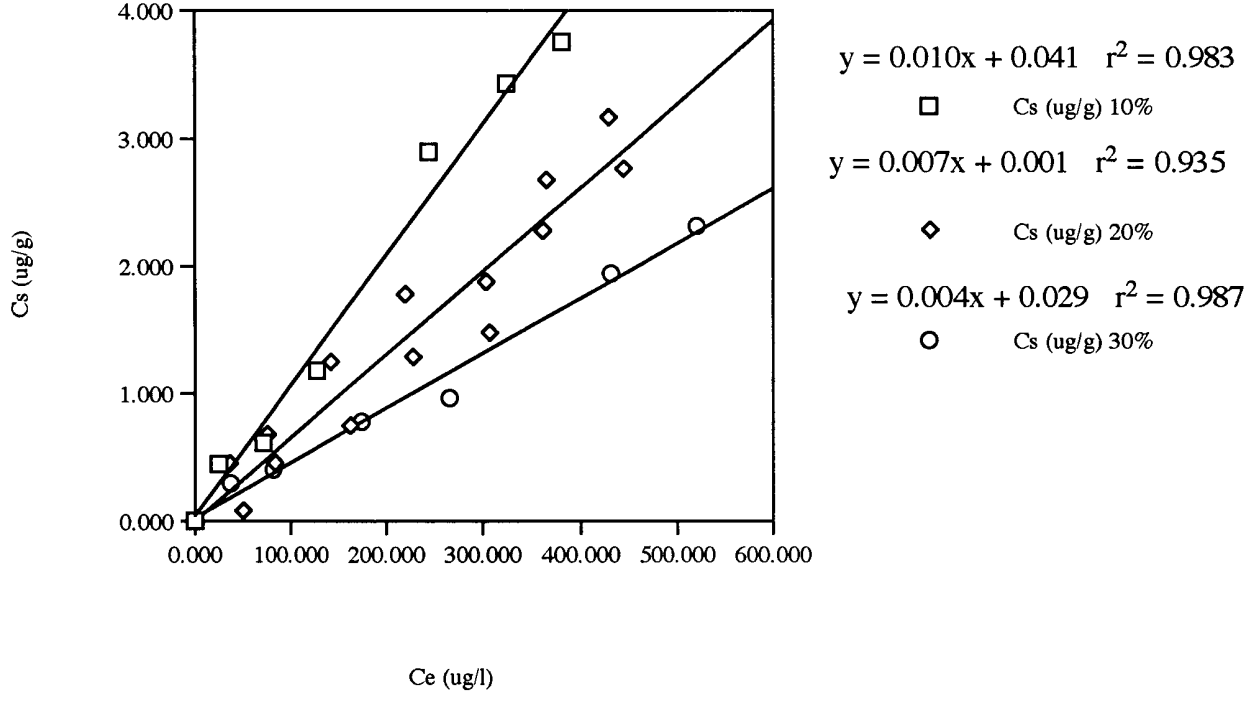


Figure 5: Rossburg Soil, effects of increased amounts of co-solvent by volume for methylnaphthlene.

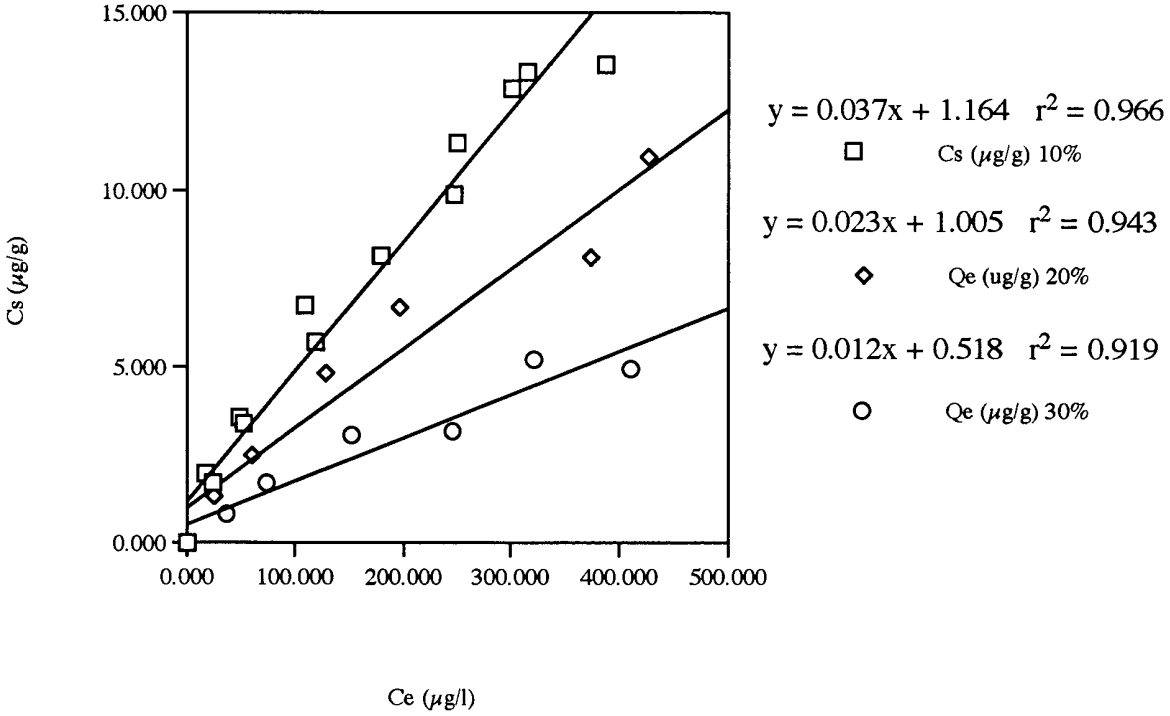
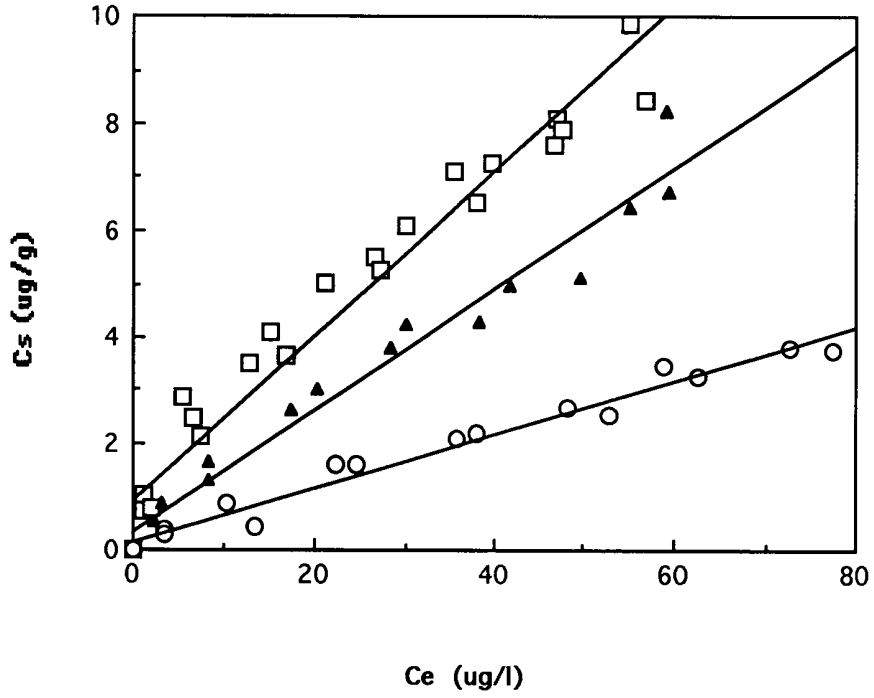


Figure 6: Rossburg Soil, effects of increased amounts of co-solvent with phenanthrene.



y = 0.94104 + 0.15453x R^2 = 0.956

□ Cs (ug/g) 10%

y = 0.35802 + 0.11401x R^2 = 0.966

▲ Cs (ug/g) 20%

y = 0.16304 + 5.0371e-2x R^2 = 0.975

○ Cs (ug/g) 30%

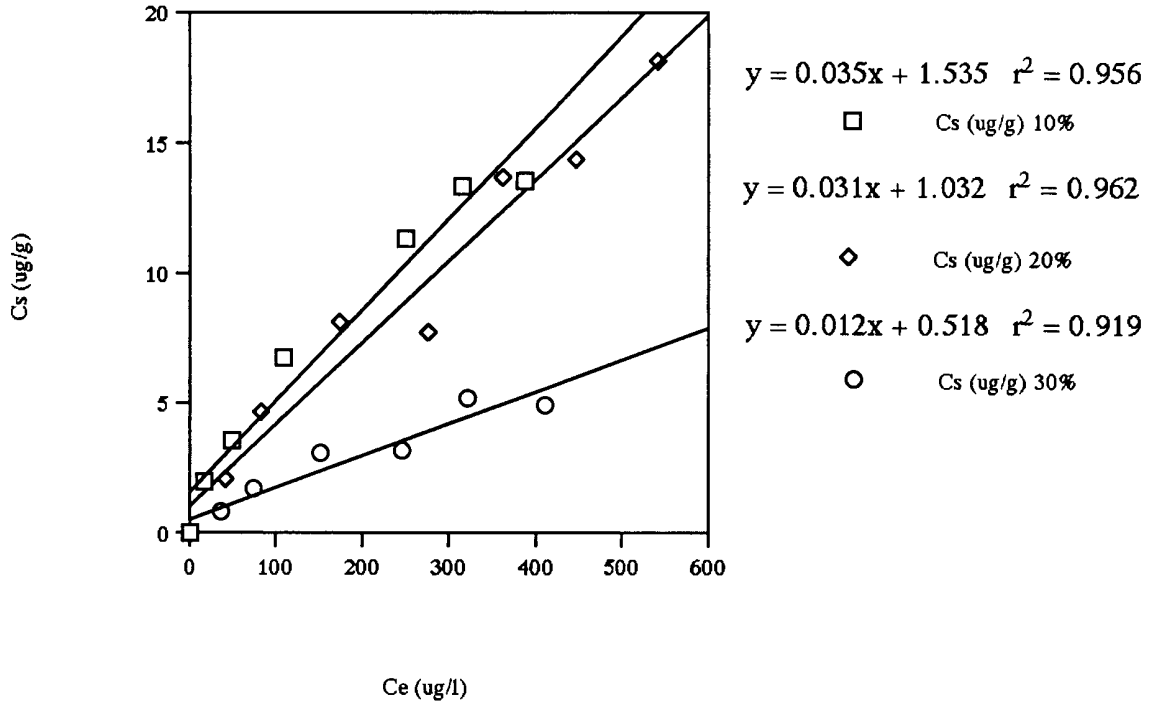


Figure 8: Piketon Soil, effects of increased amounts co-solvent with phenanthrene.

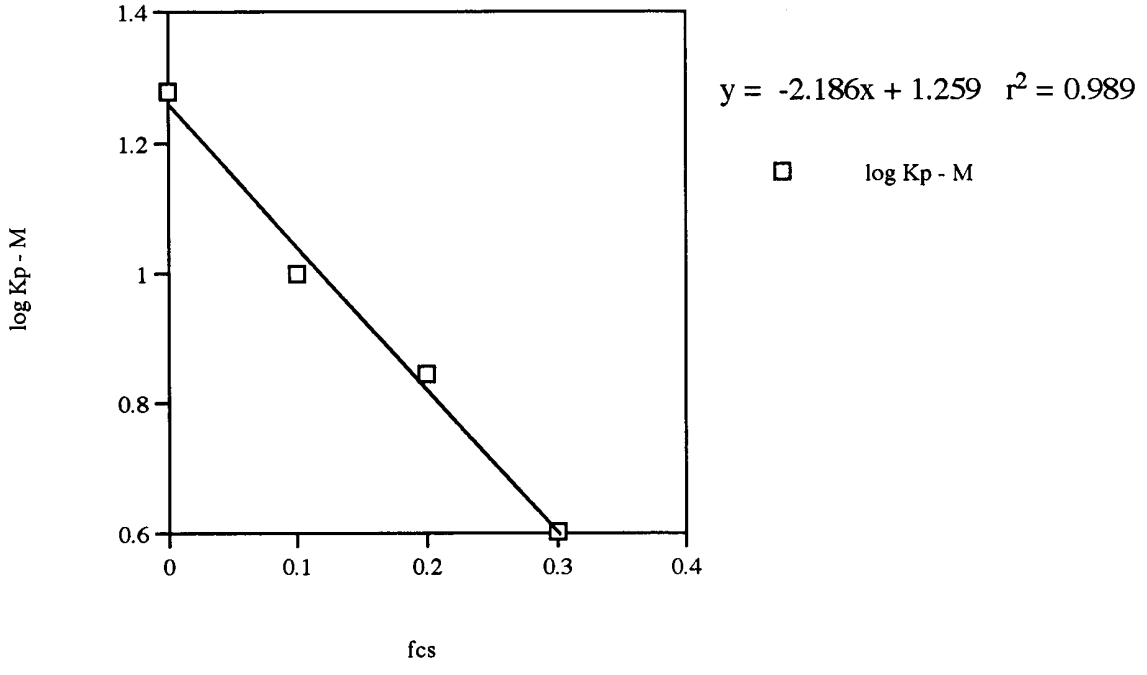


Figure 9: Plot of methylnaphthalene Kp values vs fcs for Rossburg soil.

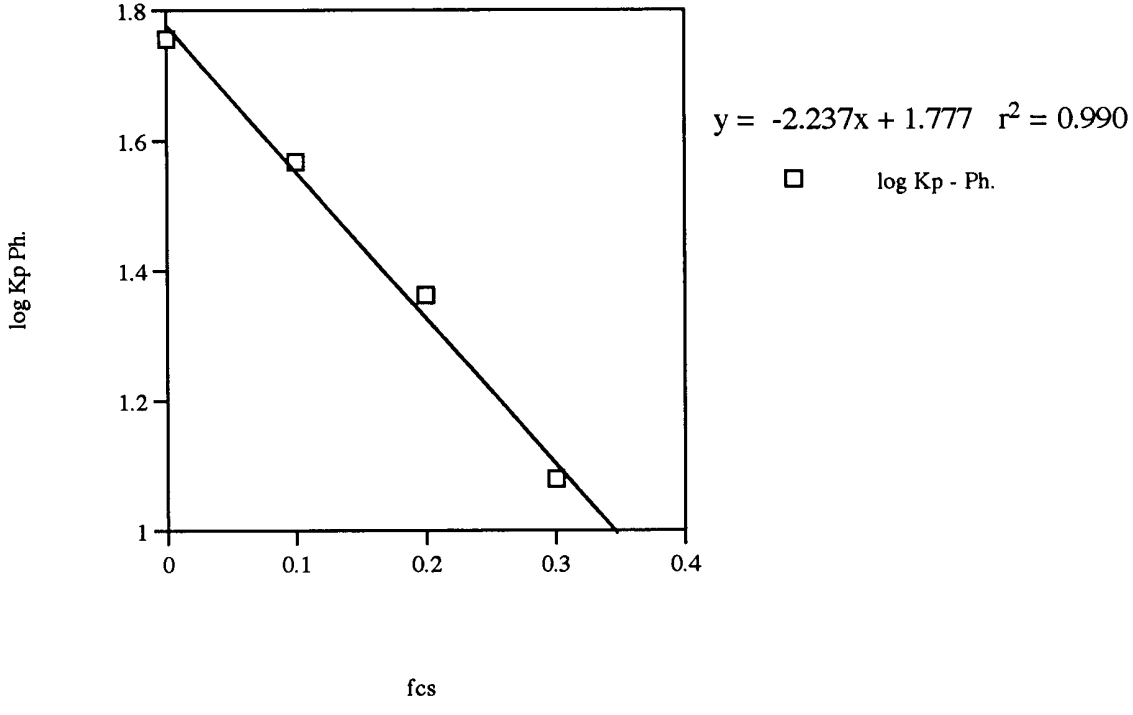


Figure 10: Plot of phenanthrene Kp values vs fcs for Roosburg soil.

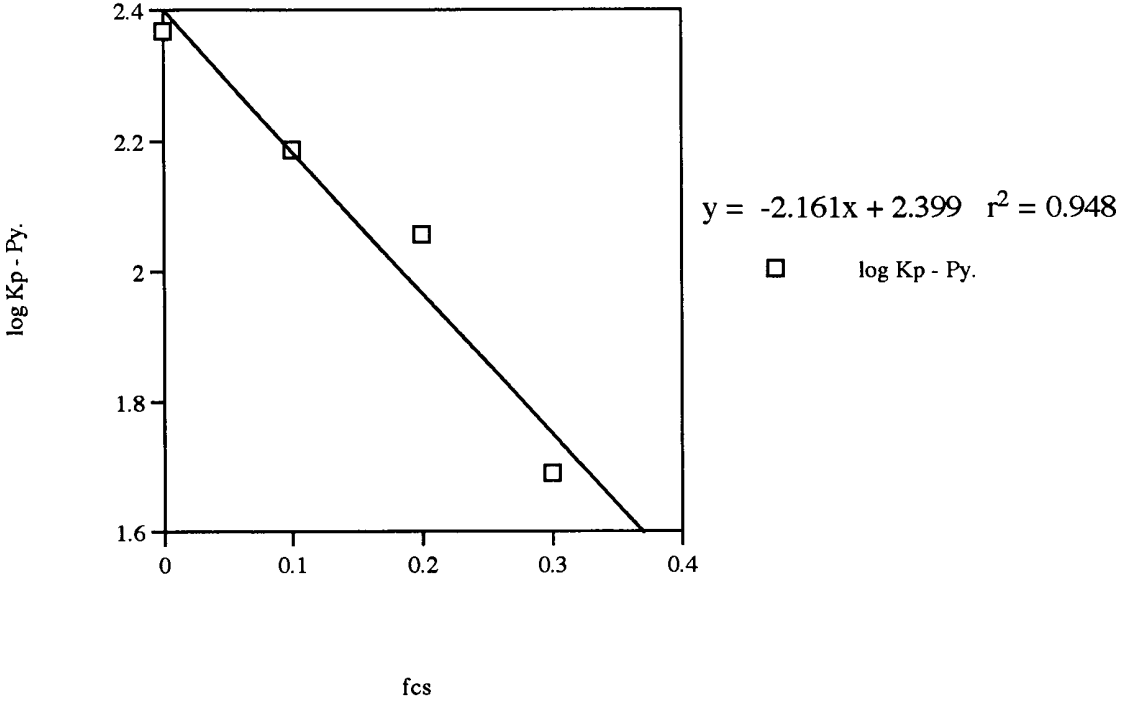


Figure 11: Plot of pyrene Kp values vs fcs for Rossburg soil.